

Efficient heat-bath sampling in Fock space

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We introduce an algorithm for sampling many-body quantum states in Fock space. The algorithm efficiently samples states with probability approximately proportional to an arbitrary function of the second-quantized Hamiltonian matrix element connecting the sampled state to the current state. We apply the new sampling algorithm to the recently-developed Semistochastic Full Configuration Interaction Quantum Monte Carlo method (S-FCIQMC), a semistochastic implementation of the power method for projecting out the ground state energy in a basis of Slater determinants. The heat-bath sampling requires modest additional computational time and memory compared to uniform sampling but results in newly-spawned weights that are approximately of the same magnitude, thereby greatly improving the efficiency of projection. A comparison in efficiency between uniform and approximate heat-bath sampling is performed on the all-electron nitrogen dimer at equilibrium in Dunning's cc-pVXZ basis sets with $X \in \{D, T, Q, 5\}$, demonstrating a large gain in efficiency that increases with basis set size. In addition, a comparison in efficiency is performed on three all-electron first-row dimers, B₂, N₂, and F₂, in a cc-pVQZ basis, demonstrating that the gain in efficiency compared to uniform sampling also increases dramatically with the number of electrons.

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I. INTRODUCTION

Methods for finding approximate solutions to the quantum many-body problem often work in Fock space, spanned by a discrete basis composed of products of N single-particle orbitals chosen from a set of M orbitals, where N is the number of particles. These products are symmetrized or antisymmetrized for bosonic or fermionic particles, respectively. However, the number of states in Fock space scales exponentially in M , and even the size of the sector of Fock space with constant particle number N sector scales combinatorially in M and N , so deterministic calculations are limited to small M and N .

When the number of states is too large for deterministic methods (approximately 10^{10}), Monte Carlo methods provide a valuable alternative. For example, the Full Configuration Interaction Quantum Monte Carlo (FCIQMC) method [1–4], and its semistochastic extension, the S-FCIQMC method [5] have been used to calculate almost exact energies in far larger state spaces. Another example is the Monte Carlo Configuration Interaction (MCCI) method [6], in which a variational wavefunction is calculated from a selected CI expansion generated by a Monte Carlo sampling procedure.

In both of these methods, Slater determinants are sampled *uniformly* from the set of determinants connected to a reference by the Hamiltonian. While uniform sampling has the advantage of being easy to implement, it is far from optimal, since some of the determinants connected to the reference are much more important than others. The definition of “importance” here depends on the method used. In S-FCIQMC, starting from an initial state, the importance of a final state is the magnitude of the Hamiltonian matrix element connecting it to the initial state: if moves are proposed with probabilities proportional to this importance function, the weight of the final state is independent of which of the possible final states is chosen. In MCCI, the importance of a state is the magnitude of the 2nd-order perturbation theory estimate of energy lowering achieved by including this state in the expansion. Since the importance of the states can range over many orders of magnitude, large gains in efficiency can be gained by sampling states in proportion to their importance. However, the naïve approach of computing the relative probabilities of all the connected states and then normalizing by dividing by their sum is prohibitively expensive because the number of connected states can be large. For example, for a quantum chemistry Hamiltonian, it scales as $\mathcal{O}(N^2M^2)$.

Motivated by the above, this paper addresses the following problem: Given an initial configuration in Fock space, how can one *efficiently* sample new configurations with probability approximately proportional to a function of the Hamiltonian matrix element connecting the new configuration to the initial one? By ‘efficient’, we mean that the time complexity of one sampling event scales as $\mathcal{O}(N)$, the same time complexity as that of computing one Hamiltonian matrix element corresponding to a single excitation in a molecular system. We also limit our storage requirements to $\mathcal{O}(M^k)$, where k is the maximum number of creation and annihilation operators in any off-diagonal term in the Hamiltonian – in other words, the same scaling as that required to store the integrals needed for computing the Hamiltonian. We take advantage of the fact that k is typically small; e.g., it is 4 for the quantum chemistry Hamiltonian and for the Hubbard model in momentum space, and it is 2 for the Hubbard model in real space. We demonstrate the efficiency gains achieved when the method is used in S-FCIQMC applied to the quantum chemistry Hamiltonian.

This paper is organized as follows. Section II has an overview of the S-FCIQMC method and its application to the quantum chemistry Hamiltonian. In Section III the approximate heat-bath sampling method is discussed within the context of S-FCIQMC. In Section IV uniform and heat-bath sampling methods are compared for S-FCIQMC calculations on the nitrogen dimer at equilibrium in several different basis sets, demonstrating that heatbath sampling is more efficient than uniform sampling by a factor that increases rapidly with basis size. Similar calculations are also performed on the boron dimer and the fluoride dimer, demonstrating that at fixed number of orbitals, the gain in efficiency increases even more rapidly with electron number.

II. BACKGROUND

A. Quantum chemistry Hamiltonian

The second-quantized nonrelativistic electronic Hamiltonian, in the Born-Oppenheimer approximation is,

$$\hat{H} = \sum_{pr} f_{rp} a_r^\dagger a_p + \frac{1}{2} \sum_{pqrs} g_{rspq} a_r^\dagger a_s^\dagger a_q a_p + h_{\text{nuc}}, \quad (1)$$

where $a_p^\dagger(a_p)$ is the usual electron creation (destruction) operator with the indices $\{p, q, r, s\}$ incorporating both spatial and spin degrees of freedom. The terms entering the expression of the Hamiltonian are,

$$f_{rp} = \int \phi_r^*(x) \left(-\frac{1}{2} \nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r}_I - \mathbf{r}|} \right) \phi_p(x) dx \quad (2)$$

the 1-center integrals with $\phi_p(x)$ denoting spin-orbitals, x the combined spatial (\mathbf{r}) and spin coordinates of the electrons, and Z_I and \mathbf{r}_I the atomic number and spatial coordinates of nucleus I ,

$$g_{rspq} = \int \phi_r^*(x_1) \phi_s^*(x_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_p(x_1) \phi_q(x_2) dx_1 dx_2 \quad (3)$$

the 2-center integrals with an index-ordering convention according to the physicist notation [7], and

$$h_{\text{nuc}} = \sum_{I < J} \frac{Z_I Z_J}{|\mathbf{r}_I - \mathbf{r}_J|} \quad (4)$$

the nuclear-nuclear repulsion. Orthogonal orbitals are used, and in the absence of a magnetic field can be chosen to be real in which case $f_{rp} = f_{pr}$ and $g_{rspq} = g_{psrq} = g_{rqps} = g_{pqrs} = g_{srqp} = g_{qrsp} = g_{spqr} = g_{qpsr}$. Hence the storage required for the 1-center integrals is $\mathcal{O}(N^2/2)$ and that for the 2-center integrals is $\mathcal{O}(N^4/8)$.

Since the Hamiltonian in Eq. (1) contains only 1-electron and 2-electron terms, it has nonzero matrix elements between two determinants only if they differ by no more than two spin-orbitals. Classifying the matrix elements by the number of spin-orbitals that the initial (i) and final states (f) differ in,

$$H_{\text{diag}} = \sum_{p \in \text{occ.}} f_{pp} + \frac{1}{2} \sum_{p, q \in \text{occ.}} (g_{ppqq} - g_{pqqp}), \quad (5)$$

$$H(r \leftarrow p) = \Gamma_{rp}^i \left(f_{rp} + \sum_{q \in \text{occ.}} (g_{rpqq} - g_{rqqp}) \right), \quad (6)$$

$$H(rs \leftarrow pq) = \Gamma_{rp}^i \Gamma_{sq}^f (g_{rspq} - g_{rsqp}), \quad (7)$$

where $\Gamma_{rp}^i = (-1)^n$, n being the number of occupied spin-orbitals between p and r in state i .

Note that the magnitudes of the matrix elements for double excitations depend only on the four spin-orbitals whose occupations are changing, though the sign depends on the other occupied spin-orbitals as well. In contrast the magnitudes of the diagonal and the single excitation matrix elements depend on all the occupied spin-orbitals.

B. S-FCIQMC overview

We now briefly review the S-FCIQMC method [5] which is a modification of the FCIQMC method [1–4]. There are three main differences between the S-FCIQMC method and the original FCIQMC method, namely, walkers have real

rather than integer weights, the computation of the mixed estimator of the energy is done using a multideterminantal trial wavefunction rather than the Hartree-Fock determinant and the part of the projection that involves the most important determinants is done deterministically rather than stochastically.

In common with all QMC methods, the S-FCIQMC method employs a “projector” operator, which is a function of the Hamiltonian such that the ground state of the Hamiltonian is the dominant state (state with largest absolute eigenvalue) of the projector. Repeated application of the projector to an arbitrary state that is not orthogonal to the ground state results in projecting onto the ground state. The S-FCIQMC method employs the linear projector,

$$\hat{G} = \hat{\mathbf{1}} + \tau \left(E_T - \hat{H} \right), \quad (8)$$

where E_T is an estimate of the ground state energy and i, j denote Fock space states. The time step, τ , must be smaller than $2/(E_{\max} - E_{\min})$, where E_{\max} and E_{\min} are the extremal eigenvalues of \hat{H} , in order for the ground state of \hat{H} to be the dominant state of \hat{G} . In order to avoid negative diagonal matrix elements in \hat{G} , τ , must be smaller than $1/(E_{\max} - E_{\min})$. In practice, τ is chosen to roughly minimize the statistical error for given computer time, and this optimal value is yet smaller.

Since the total number of states is much larger than the number of states that can be stored on a computer, it is necessary to do at least part of the projection stochastically. Before the run, a subset of the determinants is selected to be dubbed the *deterministic space*. Projection between pairs of determinants that are both in the deterministic space is performed deterministically, using a sparse matrix-vector multiplication. However, projection between a pair of determinants at least one of which is outside the deterministic space is performed stochastically, as follows.

At any Monte Carlo (MC) step, t , the current state is represented as a sparse linear combination of “occupied” states,

$$|\psi_0^t\rangle = \sum_{i \in \text{occ.}} w_i^t |i\rangle, \quad (9)$$

where w_i^t is the weight on state $|i\rangle$ at step t . The state evolves from MC step t to step $t+1$ according to

$$\begin{aligned} w_j^{t+1} &= \sum_i \hat{G}_{ji} w_i^t \\ &= \sum_i \left[\delta_{ji} + \tau \left(E_T \delta_{ji} - \hat{H}_{ji} \right) \right] w_i^t \\ &= \left(1 + \tau \left(E_T - \hat{H}_{ii} \right) \right) w_i^t - \tau \sum_{i \neq j} \hat{H}_{ji} w_i^t. \end{aligned} \quad (10)$$

Note that the first of these terms is diagonal, and the second is off-diagonal. In addition to the off-diagonal elements connecting pairs of deterministic determinants, all diagonal elements can be applied deterministically, since they do not increase the density of the sparse representation. However, the off-diagonal elements that do not connect pairs of deterministic states are sampled stochastically as follows.

On each iteration, the weight w_i^t on each Slater determinant i is divided up into an integer number of walkers $n_i^t = \max(1, \lfloor w_i^t \rfloor)$, and each walker spawns a new walker on determinant j with probability P_{ji} that receives a weight of

$$w_j^{(t+1)} = \frac{-\tau H_{ji}}{P_{ji}} \left(\frac{w_i^t}{n_i^t} \right). \quad (11)$$

To overcome the fermion sign problem, only determinants with absolute weight greater than an *initiator* threshold [2] are allowed to create weight on unoccupied determinants. The resulting bias in the energy disappears in the limit of infinite walker number. For efficiency reasons, walkers with weight less than a minimum weight are combined into a smaller number of larger weight walkers in a statistically unbiased fashion [5]. In this work, the minimum

weight is set to 0.5, and a graduated initiator is used: the initiator threshold for a given determinant is equal to the minimum number of moves a walker on that determinant has taken since its last visit to the deterministic space.

An estimate of the ground state wavefunction could in principle be obtained by summing the walker distributions over all Monte Carlo iterations over a long run, i.e.,

$$|\psi_0\rangle \approx \sum_{t=1}^{N_{\text{MC}}} |\psi_0^t\rangle = \sum_{t=1}^{N_{\text{MC}}} \sum_{i \in \text{occ.}} w_i^t |i\rangle. \quad (12)$$

However, the entire wavefunction $|\psi_0\rangle$ contains too many terms to be stored all at once; instead, only the sparse walker distribution $\{w_i^t\}$ at a given iteration can be stored. Therefore, E_0 must be estimated in a way that depends only on linear functions of the walker distributions. This is accomplished using a mixed estimator,

$$E_0^{\text{mix}} = \frac{\langle \psi_0 | \hat{H} | \psi_T \rangle}{\langle \psi_0 | \psi_T \rangle} = \frac{\sum_{t=1}^{N_{\text{MC}}} \sum_{i \in \text{occ.}} w_i^t N_i}{\sum_{t=1}^{N_{\text{MC}}} \sum_{i \in \text{occ.}} w_i^t t_i}, \quad (13)$$

where $|\psi_T\rangle = \sum_i t_i |i\rangle$ is a trial wavefunction that is chosen before the run, and $N_i = \sum_j H_{ij} t_j$ can also be computed and stored before the run. In the limit that either $|\psi_0\rangle$ or $|\psi_T\rangle$ is the exact ground state, the mixed energy is a zero-bias, zero-variance estimator of E_0 . Thus, we choose $|\psi_T\rangle$ to be a low-energy linear combination of determinants.

Before starting an S-FCIQMC run, two sets of important determinants must be selected: the deterministic space and the determinants that make up the trial wavefunction expansion (after selecting the determinants that make up $|\psi_T\rangle$, a Lanczos diagonalization is then performed within that set of determinants to obtain the coefficients). In both important subspaces, including more determinants improves the efficiency, but the two subspaces have different storage constraints. The deterministic space must be small enough that the full Hamiltonian within the deterministic space can be stored (as an upper-triangular sparse matrix). The number of determinants in $|\psi_T\rangle$ is limited by the requirement that all of the mixed energy numerators $N_i = \sum_j H_{ij} t_j$ can be stored. This means that the deterministic space can typically be much larger than the trial wavefunction expansion.

To select determinants for either subspace, the following iterative procedure is used. Starting with the Hartree-Fock determinant, all connected determinants are obtained. Second-order perturbation theory is then used to estimate the coefficient each determinant would have if a Lanczos diagonalization were performed; only the 10% of the determinants with largest expected coefficients are retained. A Lanczos diagonalization is performed in the resulting space. Then, the determinants connected to the subset of determinants with the highest absolute coefficients are obtained, and the procedure is repeated. Finally, the determinant list is truncated to the required size, and in the case of the trial wavefunction, a final Lanczos diagonalization is performed.

C. Proposal of off-diagonal moves

The computed energy does not depend on P_{ji} in Eq. 11, provided that this is in fact the probability of proposing the move. However, the statistical error does depend on P_{ji} . Large weight fluctuations increase the statistical error in any Monte Carlo calculation, and their detrimental effect is even more severe when there is a sign problem. If the new states are chosen from the *heat-bath* distribution, i.e., with probability proportional to the magnitude of the corresponding matrix element, i.e.,

$$P_{ji} = \frac{|H_{ji}|}{\sum_k |H_{ki}|}. \quad (14)$$

then their weights are independent of which state is chosen.

The difficulty with heat-bath sampling is that it is prohibitively expensive to compute the full column sum $\sum_k |H_{ki}|$ every time an off-diagonal move is proposed, since the number of off-diagonal elements is $\mathcal{O}(N^2 M^2)$. Hence, until now, most S-FCIQMC calculations have been performed using an approximately uniform sampling of

off-diagonal moves, which is computationally simpler since it only involves the number of off-diagonal elements – which can be computed before the run – rather than computing and summing them each iteration.

In this paper, we introduce an efficient new approach for sampling an approximate heat-bath distribution, in which we factor the above proposal probability into probabilities of selecting each electron and unoccupied spin-orbital separately. These probabilities of individual steps can be computed and stored before the run in order to reduce the sampling time to $\mathcal{O}(N)$, which is the same scaling as that for computing one single-excitation matrix element. The algorithm is derived in the next section, and is summarized concisely in Appendix A.

III. APPROXIMATE HEAT-BATH ALGORITHM

The nonrelativistic quantum chemistry Hamiltonian contains off-diagonal terms corresponding to single and double excitations only. Double excitations are more numerous, but much simpler to deal with than single excitations. While the number of double excitations from a given determinant is $\mathcal{O}(N^2M^2)$, the number of distinct values of double excitation matrix elements in the full Hamiltonian is only $\mathcal{O}(M^4)$, and each double excitation matrix element takes only $\mathcal{O}(1)$ time to compute. On the other hand, while the number of single excitations possible from a given determinant is only $\mathcal{O}(NM)$, the number of distinct values of single excitation matrix elements in the full Hamiltonian is combinatorially large, and each matrix element takes $\mathcal{O}(N)$ time to compute, since the matrix elements for exciting from a given spin-orbital include a sum over all other occupied spin-orbitals (see Eq. 6). So, efficient computation of single-excitation matrix elements is difficult because there are too many to store and they are expensive to compute on the fly.

Since double excitations account for most of the possible excitations from a given determinant, and since they are so much easier to deal with efficiently, we start by constructing an approximate heat-bath algorithm for double excitations, and then we incorporate single excitations into the algorithm.

A. Sampling double excitations

If single excitations are ignored, heat-bath sampling requires us to sample a move of electrons from spin-orbitals $\{p, q\}$ to spin-orbitals $\{r, s\}$ with probability

$$P(rs \leftarrow pq) = \frac{|H(rs \leftarrow pq)|}{\sum_{p'q' \in \text{occ.}} \sum_{r's' \in \text{unocc.}} |H(r's' \leftarrow p'q')|}, \quad (15)$$

where the sum over $\{p', q'\}$ is over all occupied spin-orbitals, and the sum over $\{r', s'\}$ is over all unoccupied spin-orbitals.

We can factor this probability into a four-step process as follows:

$$\begin{aligned} P(rs \leftarrow pq) &= \frac{|H(rs \leftarrow pq)|}{\sum_{p'q'} \sum_{r's'} |H(r's' \leftarrow p'q')|} \\ &= \left(\frac{\sum_{q' \in \text{occ.}} \sum_{r's' \in \text{unocc.}} |H(r's' \leftarrow pq')|}{\sum_{p'q' \in \text{occ.}} \sum_{r's' \in \text{unocc.}} |H(r's' \leftarrow p'q')|} \right) \left(\frac{\sum_{r's' \in \text{unocc.}} |H(r's' \leftarrow pq)|}{\sum_{q' \in \text{occ.}} \sum_{r's' \in \text{unocc.}} |H(r's' \leftarrow pq')|} \right) \\ &\quad \times \left(\frac{\sum_{s' \in \text{unocc.}} |H(rs' \leftarrow pq)|}{\sum_{r's' \in \text{unocc.}} |H(r's' \leftarrow pq)|} \right) \left(\frac{|H(rs \leftarrow pq)|}{\sum_{s' \in \text{unocc.}} |H(rs' \leftarrow pq)|} \right) \\ &= P(p) P(q|p) P(r|p, q) P(s|p, q, r). \end{aligned} \quad (16)$$

The conditional probabilities of selecting unoccupied spin-orbitals for double excitation, $P(r|p, q)$ and $P(s|p, q, r)$, will be different for each determinant, since they involve sums over all the spin-orbitals that are currently unoccupied.

However, we can approximate them by summing over *all* spin-orbitals, except for p and q :

$$P(r|p, q) \approx \tilde{P}(r|p, q) \equiv \frac{\sum_{s' \notin \{p, q\}} |H(rs' \leftarrow pq)|}{\sum_{rs \notin \{p, q\}} |H(rs' \leftarrow pq)|}, \quad P(s|p, q, r) \approx \tilde{P}(s|p, q, r) \equiv \frac{|H(rs \leftarrow pq)|}{\sum_{s' \notin \{p, q\}} |H(rs' \leftarrow pq)|}. \quad (17)$$

Spin-orbitals can be sampled from these distributions in $\mathcal{O}(1)$ time using the alias method [8], as described in Appendix D.

A similar approximation can be made for the probability of selecting the occupied spin-orbitals, $P(p)$ and $P(q|p)$. Defining

$$D_{pq} \equiv \sum_{r's' \notin \{p, q\}} |H(r's' \leftarrow pq)| \quad \text{and} \quad S_p \equiv \sum_{q' \neq p} D_{pq'}, \quad (18)$$

we can approximate $P(p)$ and $P(q|p)$ by

$$P(p) \approx \tilde{P}(p) \equiv \frac{S_p}{\sum_{p' \in \text{occ.}} S_{p'}}, \quad P(q|p) \approx \tilde{P}(q|p) \equiv \frac{D_{pq}}{\sum_{q' \in \text{occ.}} D_{pq'}}. \quad (19)$$

Since S_p , D_{pq} , $\tilde{P}(r|p, q)$, and $\tilde{P}(s|p, q, r)$ all involve sums over *all* spin-orbitals, they can be computed and stored once at the beginning of the run. However, $\tilde{P}(p)$ and $\tilde{P}(q|p)$ involve sums over only the currently-occupied spin-orbitals, and thus they must be computed on the fly (in $\mathcal{O}(N)$ time).

Note that approximating the heat-bath probabilities affects only the efficiency of the calculation, not its exactness. Once the initiator bias has been extrapolated away, the results are exact (i.e., they have a statistical error but no bias), so long as the same probabilities are used for proposing moves and computing the weights.

B. Sampling single excitations

We now modify the double-excitation proposal algorithm above to include the possibility of proposing a single excitation. After selecting electrons in spin-orbitals $\{p, q\}$ and empty spin-orbital r , we allow two possibilities:

1. Select a second unoccupied spin-orbital s , generating the double excitation $(rs \leftarrow pq)$ (as described above),
OR
2. Discard the already-selected occupied spin-orbital q and generate the single excitation $(r \leftarrow p)$.

The heat-bath distribution requires us to choose between a single and a double excitation with probability proportional to their corresponding matrix elements:

$$P(\text{single}|p, q, r) \propto |H(r \leftarrow p)|, \quad \text{and} \quad P(\text{double}|p, q, r) \propto H_{rpq}^{\text{tot}}, \quad (20)$$

where

$$H_{rpq}^{\text{tot}} \equiv \sum_{s' \notin \{p, q, r\}} |H(rs' \leftarrow pq)| \quad (21)$$

is the sum of double-excitation off-diagonal elements in which electrons in spin-orbitals p and q excite to two *other* spin-orbitals, one of which is r . Note that H_{rpq}^{tot} can be precomputed and stored at the beginning of the run.

One method of choosing between single and double excitations is to choose a single excitation with probability $\frac{|H(r \leftarrow p)|}{H_{rpq}^{\text{tot}} + |H(r \leftarrow p)|}$ and to choose a double excitation otherwise. However, the problem with this approach is that if

$|H(r \leftarrow p)| \gg H_{rpq}^{\text{tot}}$ the double excitation probability becomes small, so when a double excitation is chosen, the newly-spawned walker gets a large weight. A solution to this problem is to make both a double-excitation and a single-excitation move if $|H(r \leftarrow p)| > H_{rpq}^{\text{tot}}$. Using this approach, the probabilities of selecting a single or double excitation are

$$\tilde{P}(\text{single}|p, q, r) = \begin{cases} \frac{|H(r \leftarrow p)|}{H_{rpq}^{\text{tot}} + |H(r \leftarrow p)|}, & \text{if } |H(r \leftarrow p)| < H_{rpq}^{\text{tot}}; \\ 1, & \text{otherwise,} \end{cases} \quad (22)$$

and

$$\tilde{P}(\text{double}|p, q, r) = \begin{cases} \frac{H_{rpq}^{\text{tot}}}{H_{rpq}^{\text{tot}} + |H(r \leftarrow p)|}, & \text{if } |H(r \leftarrow p)| < H_{rpq}^{\text{tot}}; \\ 1, & \text{otherwise,} \end{cases} \quad (23)$$

respectively. Now, there can still be some large-weight single-excitation moves when $|H(r \leftarrow p)| \gg H_{rpq}^{\text{tot}}$, but since single-excitation moves are a very small fraction of all moves, this is not a serious problem.

C. Check for correctness of heat-bath sampling

While all valid double excitations can be proposed using this algorithm, one may wonder whether the same is true of single excitations. The only situation in which a valid single excitation ($r \leftarrow p$) cannot be proposed by our heat-bath algorithm is if all other occupied spin-orbitals $q \neq p$ are the only ones of their irreducible representation, since then there would be no symmetry-allowed double excitation ($rs \leftarrow pq$), and $\tilde{P}(r|p, q)$ would be zero. Hence, a sufficient – but not necessary – condition for heat-bath sampling to be correct for a given system consisting of n_{\uparrow} spin-up electrons and n_{\downarrow} spin-down electrons is:

$$\max(n_{\uparrow}, n_{\downarrow}) > N'_{\text{irrep}}, \quad (24)$$

where N'_{irrep} is the number of irreducible representations consisting of only one spatial orbital.

Care must be taken that the full symmetry is used in this step. It is common practice to use D_{2h} symmetry, rather than the full $D_{\infty h}$ symmetry, for a homonuclear diatomic molecule. For example, suppose there is only one orbital pair that transforms as the Δ_g irreducible representation of $D_{\infty h}$. The member of the pair that transforms as $x^2 - y^2$ belongs to the A_g irreducible representation of D_{2h} whereas the member that transforms as xy belongs to the B_{1g} irreducible representation of D_{2h} . However, there are other functions, 1, $x^2 + y^2$ and z^2 that also transform as the A_g representation. So, using the irreducible representations of $D_{\infty h}$ we would conclude that this orbital pair contributes two to N'_{irrep} , whereas using the irreducible representations of D_{2h} symmetry we would incorrectly conclude that this orbital pair contributes one to N'_{irrep} .

In practice, when we do not know the irreducible representations of the orbitals in the full symmetry group, we calculate N'_{irrep} as follows. Consider the system consisting of the same set of M spatial orbitals but only one electron. Compute the Full CI Hamiltonian matrix H' (dimension M) for this system. The number of columns of H' that have no nonzero off-diagonal elements is equal to N'_{irrep} . This check is done at the beginning of a run to ensure that heat-bath sampling is unbiased for the system being examined.

IV. RESULTS: B₂, N₂ AND F₂ MOLECULES

The relative efficiency of the approximate heat-bath method to the uniform method was tested on the B₂, N₂ and F₂ molecules. Dunning's cc-pVQZ basis was used for all three molecules, and in addition, for N₂, cc-pVXZ bases with $X \in \{\text{D, T, Q, 5}\}$ were used to study the basis set dependence. For each basis set, the determinants in both the deterministic space and the trial wavefunction were selected from the set of determinants that are at most quadruple excitations from the Hartree-Fock determinant. The size of the deterministic space was 4×10^4 determinants, and

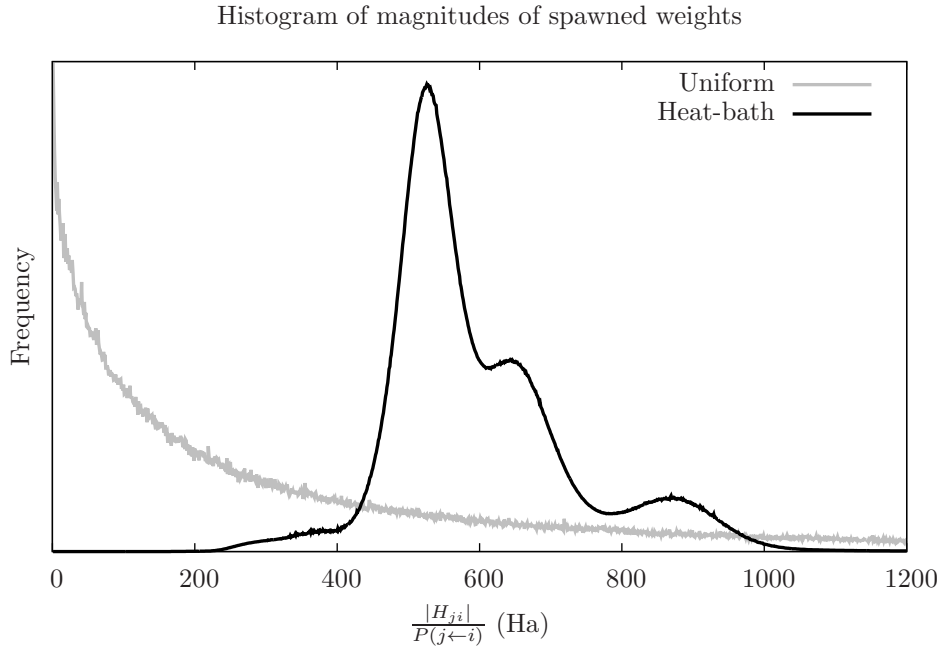


FIG. 1. Probability distributions of off-diagonal absolute weights (in multiples of τ), spawned by the uniform and heat-bath algorithms for equilibrium N_2 in a cc-pV5Z basis at with all electrons excited and 10^6 walkers. In the new heat-bath sampling algorithm, the spawned off-diagonal weights are close in magnitude, whereas in uniform sampling, the values of the spawned weights span many orders of magnitude. The location of the peak in the heat-bath distribution corresponds to an off-diagonal weight of about 0.1.

the trial wavefunction contained 10^3 determinants (except for cc-pV5Z, which had a trial wavefunction with only 500 determinants). To accelerate convergence, time-reversal symmetry (see Appendix E) and natural orbitals from a second-order Moller-Plesset perturbation theory (MP2) calculation were used.

Fig. 1 shows the frequency of spawned absolute weights (in units of τ) for the uniform and the approximate heat-bath methods applied to the N_2 molecule at equilibrium geometry in a cc-pV5Z basis. The vast majority of the absolute weights spawned by the heat-bath method lie in the range 250-1000 Ha times τ , whereas those spawned by the uniform method range over orders of magnitude.

The reduction in the spread of the spawned weights makes the initiator approximation [2] more meaningful and allows one to use a larger time step τ . In the uniform method, a state can become an initiator simply because it happened to receive a large weight from a single determinant. The increase in τ speeds up the time needed to achieve equilibration, as well as increasing the efficiency of the method. Since the statistical uncertainty, σ_E , in the estimate of the ground state energy decreases as the inverse square root of the Monte Carlo run time T , the efficiency is defined to be

$$\text{Efficiency} \propto \frac{1}{\sigma_E^2 T}. \quad (25)$$

We note that unlike the diffusion Monte Carlo method where the equilibration time is a negligible part of the total time, in S-FCIQMC the equilibration can be a substantial part of the total.

Table I shows these quantities for a sequence of three molecules. The efficiency gain increases with the number of electrons from 3.8 for B_2 , to 54 for F_2 . For uniform sampling, when N or M is large, it is hard to get an accurate estimate of the statistical error because (1) the optimal τ is very small, making the autocorrelation time in units of the number of Monte Carlo steps very long, and (2) the population must be sufficiently large to enable cancellations to occur. Thus, in Tables I and II, the equilibration speedup and increase in optimal time step are given to only single-digit accuracy.

Table II demonstrates that the efficiency gain increases with the size of the basis. For the N_2 molecule, the gain increases from 3.4 for the cc-pVDZ basis to 32 for the cc-pV5Z basis. For the cc-pV5Z basis, Fig. 2 shows how the

molecule	efficiency gain	equilibration speedup	τ_{opt} increase
B ₂	3.8	5	20
N ₂	31	30	200
F ₂	54	50	200

TABLE I. Efficiency gains for all-electron equilibrium calculations of the ground state energy in a cc-pVQZ basis for different molecules. The efficiency gain increases with the number of electrons.

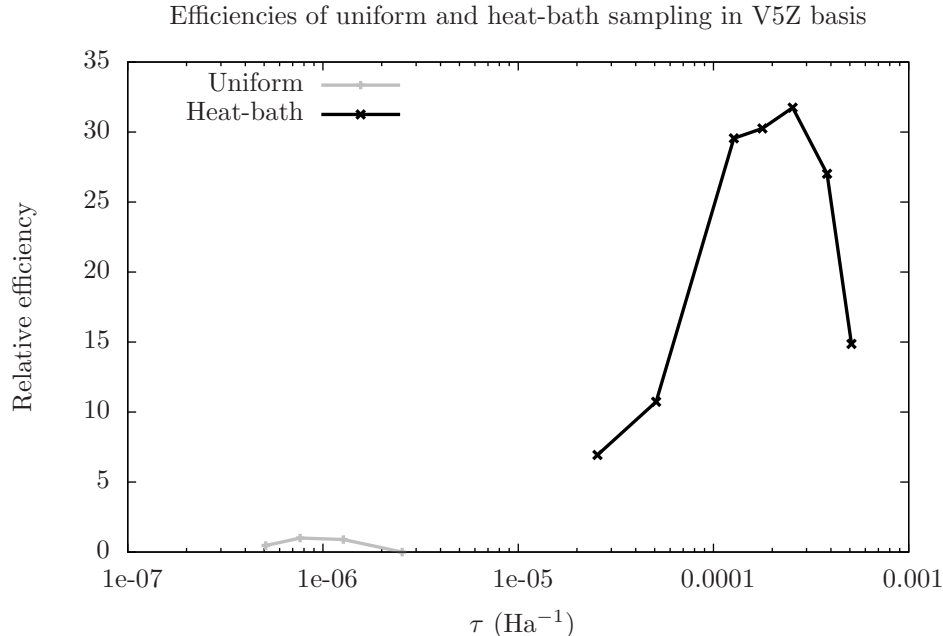


FIG. 2. Comparison of relative efficiency vs. time step size for uniform and heat-bath methods on the all-electron nitrogen dimer at equilibrium in the cc-pV5Z basis. Efficiency plotted relative to the greatest efficiency seen for uniform. Heat-bath sampling improves efficiency by a factor of 32, while the optimal time step is about a factor of 300 larger.

relative efficiencies change with τ . The relative efficiencies are normalized such that the peak for uniform sampling is at one. Not only is the peak efficiency 32 times higher for heat-bath sampling, but the peak is broader, which makes it easier to choose a value of τ that is close to optimal.

basis	efficiency gain	equilibration speedup	τ_{opt} increase
cc-pVDZ	3.4	2	5
cc-pVTZ	16	30	200
cc-pVQZ	31	30	200
cc-pV5Z	32	60	300

TABLE II. Efficiency gains and the factor by which the optimal time step τ_{opt} increases upon using heat-bath sampling instead of uniform sampling, for N₂ at the equilibrium geometry including core excitations. For a given sampling algorithm, τ_{opt} is the time step that maximizes the efficiency. The gain in efficiency of heat-bath sampling over uniform sampling increases with increasing basis set size.

In summary, the gain in efficiency from using heat-bath sampling rather than uniform sampling increases both with the number of electrons and the number of spin-orbitals.

V. DISCUSSION

The approximate heat-bath sampling algorithm introduced in this paper enables one to sample many-body quantum states connected to an initial state with probability approximately proportional to an arbitrary function

of the Hamiltonian matrix element connecting the two states. We chose the probabilities to be proportional to the corresponding matrix element, which greatly improves the efficiency of S-FCIQMC. However, other choices are possible; e.g., in the Monte Carlo Configuration Interaction method [6], it would be useful to choose the probabilities to be proportional to the lowering in energy estimated from second-order perturbation theory.

Finally, we note that the gain in efficiency from using the heat-bath method will be even greater for excited states if they are calculated using a projector that involves sampling the square of the Hamiltonian [9], since products of weights fluctuate even more than the weights themselves.

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Appendix A: Recap of algorithm when applied to S-FCIQMC

Before the S-FCIQMC run, compute and store the quantities S_p , D_{pq} , $\tilde{P}(r|p, q)$, $\tilde{P}(s|p, q, r)$, and H_{rpq}^{tot} , as described in Appendix C.

When spawning off-diagonal moves from determinant $|i\rangle$, first compute and store the probability distribution for selecting the first occupied spin-orbital p from this determinant,

$$\tilde{P}(p) = \frac{S_p}{\sum_{p'} S_{p'}}, \quad (\text{A1})$$

and compute the A and Q arrays needed for the alias method (see Appendix D). This step takes $\mathcal{O}(N)$ time.

Divide up the weight w_i on $|i\rangle$ into $n_i = \max(1, \lfloor |w_i| \rfloor)$ walkers. Then, for each walker on determinant $|i\rangle$, spawn one or two new determinants as follows:

1. Using the alias method, choose the first occupied spin-orbital p from the stored distribution $\tilde{P}(p)$. This step takes $\mathcal{O}(1)$ time.
2. Compute the probability distribution for choosing the second occupied spin-orbital q given that p was already selected,

$$\tilde{P}(q|p) = \frac{D_{pq}}{\sum_{q'} D_{pq'}}, \quad (\text{A2})$$

and sample the second occupied spin-orbital q from $\tilde{P}(q|p)$. This step takes $\mathcal{O}(N)$ time.

3. Choose a spin-orbital $r \notin \{p, q\}$ from the stored distribution $\tilde{P}(r|p, q)$, such that p and r are of the same spin, using the alias method. If r is occupied in $|i\rangle$, no moves are generated by this walker; go to next walker. Otherwise, r is the first unoccupied spin-orbital for this excitation. This step takes $\mathcal{O}(1)$ time.
4. Decide whether to spawn a single excitation, a double excitation or one of each, as follows. Compute the single-excitation matrix element $H(r \leftarrow p)$. If $|H(r \leftarrow p)|$ is greater than the stored quantity H_{rpq}^{tot} , then spawn both the single excitation ($r \leftarrow p$) and a double excitation; otherwise spawn only one of the two types of excitations as follows. With probability

$$\frac{|H(r \leftarrow p)|}{H_{rpq}^{\text{tot}} + |H(r \leftarrow p)|}, \quad (\text{A3})$$

choose the single excitation ($r \leftarrow p$); otherwise choose a double excitation. This step takes $\mathcal{O}(N)$ time, since that is the complexity of computing a single-excitation matrix element.

5. If a double excitation is to be proposed, choose a fourth spin-orbital $s \notin \{p, q, r\}$ from the stored distribution $\tilde{P}(s|p, q, r)$, using the alias method. If s is occupied in $|i\rangle$, no double excitation is generated by this walker. Otherwise, s is the second unoccupied spin-orbital for this excitation, and the move $(rs \leftarrow pq)$ is generated. This step takes $\mathcal{O}(1)$ time.
6. After generating the excitation(s), compute the weight spawned on the new determinant(s) as follows. If a single excitation $(r \leftarrow p)$ was proposed to a new determinant $|j\rangle$, the weight spawned on $|j\rangle$ is

$$w_j^{(t+1)} = \frac{-\tau H(r \leftarrow p)}{P(r \leftarrow p)} \left(\frac{w_i^t}{n_i} \right), \quad (\text{A4})$$

where $P(r \leftarrow p)$ is given in Appendix B. If a double excitation $(rs \leftarrow pq)$ was proposed to a new determinant $|k\rangle$, the weight spawned on $|k\rangle$ is

$$w_k^{(t+1)} = \frac{-\tau H(rs \leftarrow pq)}{P(rs \leftarrow pq)} \left(\frac{w_i^t}{n_i} \right), \quad (\text{A5})$$

where $P(rs \leftarrow pq)$ is given in Appendix B.

Appendix B: Proposal probabilities

As discussed in the text, when a new walker is spawned, the weight assigned to that walker is proportional to the corresponding matrix element of the projector divided by the proposal probability for that transition. The computation of these proposal probabilities is described next. The proposal probabilities both for single and double excitations can be computed in $\mathcal{O}(N)$ time.

1. Single excitations

The probability for a single excitation $(r \leftarrow p)$ is

$$P(r \leftarrow p) = \sum_{q' \in \text{occ.}} \tilde{P}(p) \tilde{P}(q'|p) \tilde{P}(r|p, q') \tilde{P}(\text{single}|p, q, r), \quad (\text{B1})$$

where

$$P(\text{single}|p, q, r) = \begin{cases} \frac{|H(r \leftarrow p)|}{H_{rpq}^{\text{tot}} + |H(r \leftarrow p)|}, & \text{if } |H(r \leftarrow p)| < H_{rpq}^{\text{tot}}; \\ 1, & \text{otherwise,} \end{cases} \quad (\text{B2})$$

is the probability of choosing the single excitation $(r \leftarrow p)$ given that spin-orbitals $\{p, q, r\}$ have already been selected.

An alternative probability is $P'(r \leftarrow p) = (N-1) \tilde{P}(p) \tilde{P}(q|p) \tilde{P}(r|p, q)$, where q is the spin-orbital that was selected and discarded during the heat-bath sampling routine. As described in Appendix F, this alternative method has an efficiency tradeoff associated with it: it increases efficiency by avoiding having to compute all terms in the sum, but it also decreases efficiency by increasing the fluctuations in spawned weights. This alternative probability was not employed in this paper.

2. Double excitations

The probability for a double excitation ($rs \leftarrow pq$) is

$$P(rs \leftarrow pq) = \tilde{P}(p) \tilde{P}(q|p) \left[\tilde{P}(r|p, q) \tilde{P}(\text{double}|p, q, r) \tilde{P}(s|p, q, r) + \tilde{P}(s|p, q) \tilde{P}(\text{double}|p, q, s) \tilde{P}(r|p, q, s) \right] \\ + \tilde{P}(q) \tilde{P}(p|q) \left[\tilde{P}(r|q, p) \tilde{P}(\text{double}|q, p, r) \tilde{P}(s|q, p, r) + \tilde{P}(s|q, p) \tilde{P}(\text{double}|q, p, s) \tilde{P}(r|q, p, s) \right], \quad (\text{B3})$$

where

$$\tilde{P}(\text{double}|p, q, r) = \begin{cases} \frac{H_{rpq}^{\text{tot}}}{H_{rpq}^{\text{tot}} + |H(r \leftarrow p)|}, & \text{if } |H(r \leftarrow p)| < H_{rpq}^{\text{tot}}, \\ 1, & \text{otherwise,} \end{cases} \quad (\text{B4})$$

is the probability of choosing a double excitation given that $\{p, q, r\}$ have already been selected.

The second and third terms in Eq. B3 are zero for opposite-spin excitations.

As with single excitations, an alternative probability is

$$P'(rs \leftarrow pq) = c \tilde{P}(p) \tilde{P}(q|p) \tilde{P}(r|p, q) \tilde{P}(\text{double}|p, q, r) \tilde{P}(s|p, q, r) \tilde{P}(p) \tilde{P}(q|p) \tilde{P}(r|p, q), \quad (\text{B5})$$

where c is either 2 or 4 for opposite-spin or same-spin double excitations, respectively. Again, this alternative probability was not employed in this paper.

Appendix C: Quantities that must be precomputed at start of run

At the start of the run, compute and store the following tensors. It is assumed that up- and down-spin orbitals are the same, but the number of up- and down-spin electrons need not be the same.

1. Electron pair selection probabilities tensor:

$$D_{pq} = \sum_{r's'} |H(r's' \leftarrow pq)| \quad (\text{C1})$$

for all $p \neq q$. If single excitations were ignored, this would roughly correspond to the relative heat-bath probability of selecting a pair of electrons to excite, i.e., $\tilde{P}(p, q) \propto D_{pq}$. This has size $2M(2M - 1)/2$, since electrons can be of either spin. The storage could be reduced to $M(M - 1)/2$ for same-spin electrons and M^2 for opposite-spin electrons.

2. Single electron selection probabilities tensor:

$$S_p = \sum_{q' \neq p} D_{pq'} \quad (\text{C2})$$

for all p . The electrons are chosen one at a time with probabilities $\tilde{P}(p)$ and $\tilde{P}(q|p)$ computed using S_p and D_{pq} , respectively. S has size M .

3. First hole selection probabilities tensor:

$$\tilde{P}(r|p, q) = \frac{\sum_{s'} |H(rs' \leftarrow pq)|}{\sum_{r's'} |H(r's' \leftarrow pq)|} \quad (\text{C3})$$

for all $p \neq q \neq r$. This is the probability of choosing the first empty spin-orbital r , given that electrons in spin-orbitals p and q have already been selected for excitations. This can be stored as two separate tensors, $\tilde{P}_{\text{same}}(r|p, q)$ and $\tilde{P}_{\text{opposite}}(r|p, q)$, for same-spin and opposite-spin double excitations, respectively. The same-spin excitation tensor only has to be of size $\frac{1}{2}M^3$, while the opposite-spin excitation tensor can be of size M^3 . In that case, $\tilde{P}_{\text{opposite}}(r|p, q)$ represents the probability of choosing r given p, q with r and p having same spin.

4. Double excitations probabilities tensor:

$$\tilde{P}(s|p, q, r) = \frac{|H(rs \leftarrow pq)|}{\sum_{s'} |H(rs' \leftarrow pq)|} \quad (\text{C4})$$

for all $p \neq q \neq r \neq s$. When sampling a double excitation, this is the probability of choosing the second empty spin-orbital s given that electrons in spin-orbitals p and q and empty spin-orbital r have already been chosen. Also, store the denominators $H_{rpq}^{\text{tot}} = \sum_{s'} |H(rs' \leftarrow pq)|$, the summed magnitudes of double excitation matrix elements. This will be needed for comparing with single excitation matrix elements. The tensor can be stored as two separate tensors, $\tilde{P}_{\text{same}}(s|p, q, r)$ and $\tilde{P}_{\text{opposite}}(s|p, q, r)$, of sizes $\frac{1}{2}M^4$ and M^4 , respectively.

For each of the two probability tensors $\tilde{P}(r|p, q)$ and $\tilde{P}(s|p, q, r)$, we store not only the probabilities, but the corresponding A and Q tensors for sampling them in $\mathcal{O}(1)$ time using the alias method (see Appendix D). Thus, the total storage space for $\tilde{P}(s|p, q, r)$ and its corresponding A and Q tensors is $\frac{3}{2}M^4$ integers and $3M^4$ single-precision real numbers. In comparison, the integrals files that are already being stored are $\mathcal{O}(\frac{1}{8}M^4)$ double-precision real numbers, so the storage requirement is 18 times larger than the storage requirement for the integrals alone.

1. Relaxing the storage requirements

While the above storage requirements have the same $\mathcal{O}(M^4)$ scaling as the two-body integrals that are already stored, the fact that $\tilde{P}(s|p, q, r)$ requires 18 times the storage of the integrals can become prohibitive for more than about 250 orbitals. One possibility is to make a Cauchy-Schwarz approximation for estimating the 2-body integrals [10]. Instead, here we discuss a method that avoids storing $\tilde{P}(s|p, q, r)$ for all $\mathcal{O}(M^4)$ combinations $\{p, q, r, s\}$ without making the Cauchy-Schwarz approximation.

First, note that $\tilde{P}(s|p, q, r)$ is only sampled when $\{p, q, r\}$ have already been selected. Some $\{p, q, r\}$ combinations occur a lot more often than others, so $\tilde{P}(s|p, q, r)$ needs to be stored only for the most frequently-occurring triplets $\{p, q, r\}$. For the other, less frequently-occurring triplets $\{p, q, r\}$, one could either choose spin-orbital s uniformly, or compute the correct heat-bath conditional probability $P(s|p, q, r)$ on the fly in $\mathcal{O}(M)$ time.

As can be seen in Fig. 3, the fraction of $\{p, q, r\}$ triplets that account for the vast majority of calls to sample $\tilde{P}(s|p, q, r)$ decreases with basis set size. In order to account for 99% of the number of calls to sample $\tilde{P}(s|p, q, r)$, for cc-pVDZ, one must store $\tilde{P}(s|p, q, r)$ for about 50% of the $\{p, q, r\}$ triplets, while for cc-pV5Z, it is only required to store $\tilde{P}(s|p, q, r)$ for about 20% of the triplets.

The largest basis used in this paper is cc-pV5Z (182 orbitals), but with this modification, calculations with a cc-pV6Z basis (280 orbitals) could easily be done.

Appendix D: Alias method for sampling from discrete distributions

Discrete distributions consisting of M probabilities can be sampled straightforwardly by constructing an array of cumulative probabilities, drawing a random number, and doing a binary search to find the interval in which the random number falls. This requires $\mathcal{O}(M)$ time to set up the cumulative probabilities and $\mathcal{O}(\log M)$ time to sample.

However, when the same distribution is being sampled repeatedly, the alias method [8] can be used to sample it in even more quickly, in $\mathcal{O}(1)$ time. The method employs a real array, Q , and an integer array A , each of length M . Sampling with the alias method is done as follows. First, orbital i is selected uniformly from the set of all M

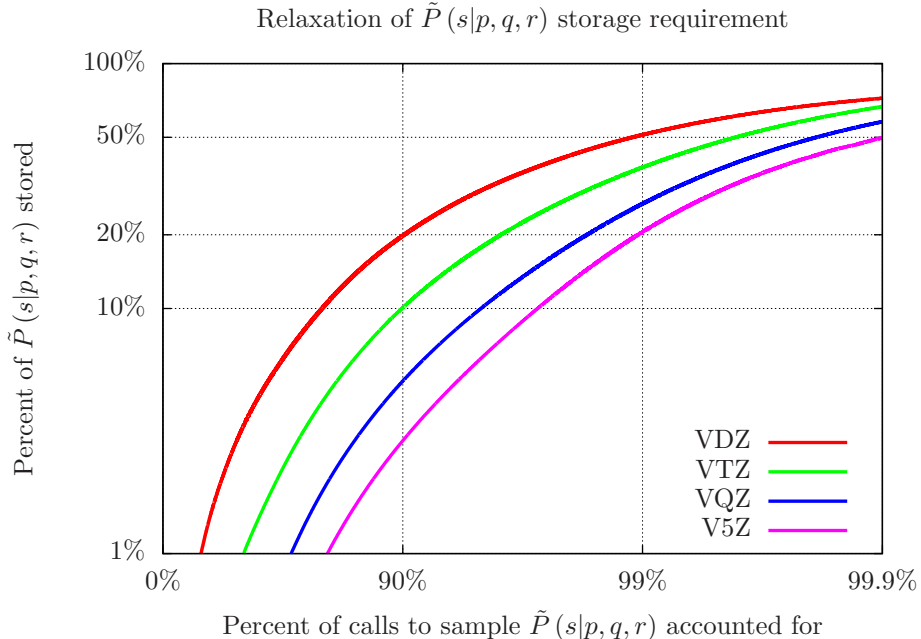


FIG. 3. This plot shows what percentage of $\tilde{P}(s|p, q, r)$ must be stored, in order for the stored part of $\tilde{P}(s|p, q, r)$ to account for a given percentage of the total calls to sample it, for an all-electron nitrogen dimer in cc-pVXZ basis sets for $X \in \{D, T, Q, 5\}$. It was obtained by counting the number of times that each triplet $\{p, q, r\}$ was selected (followed by sampling $\tilde{P}(s|p, q, r)$) during a run with 10^5 walkers.

possible orbitals. Then, with probability Q_i , orbital i is sampled; else, orbital A_i is sampled. The cost of doing this is just the cost of drawing two uniform random numbers.

The set of probabilities $\{Q_i\}$ and aliases $\{A_i\}$ can be generated in $\mathcal{O}(M)$ time at the beginning of the run [11] as shown in the pseudocode in Fig. 4.

Appendix E: Time-reversal symmetry

The size of the Hilbert space can be reduced by almost a factor of two when the number of up and down electrons are equal by taking advantage of time-reversal symmetry. This increases the effectiveness of cancellations, and allows one to use larger deterministic spaces and trial wavefunctions in S-FCIQMC. It also enables one to calculate an excited state as easily as the ground state provided that it is the lowest state of a different symmetry under time reversal than the ground state; e.g., if the ground state is a singlet, it enables calculating the lowest triplet state. All calculations in this paper make use of time-reversal symmetry and here we discuss details of how it is implemented in S-FCIQMC.

Let \hat{T} denote the time-reversal operator, so $|i'\rangle \equiv \hat{T}|i\rangle$ is the state obtained by flipping all the spins of the electrons in state $|i\rangle$. Since $\hat{T}^2|i\rangle = |i\rangle$, the eigenvalues of the time-reversal operator, z , must be ± 1 . Even S states have $z = 1$, and odd S states have $z = -1$, where S is the total spin of the system. So, the wavefunctions can be expanded in a symmetrized basis,

$$|\tilde{i}\rangle = \frac{1}{\sqrt{2N_i}} (|i\rangle + z|i'\rangle) \quad (\text{E1})$$

where,

$$N_i = \begin{cases} 1, & \text{if } \langle i|i'\rangle = 0, \\ \sqrt{2}, & \text{otherwise,} \end{cases} \quad (\text{E2})$$

FIG. 4. Alias method setup

```

! Inputs:  M = number of discrete states to sample
!          {P(i)} = discrete set of probabilities of sampling state i
!
! Outputs: {A(i)} = aliases of states
!          {Q(i)} = probabilities of returning state i rather than its alias A(i)

! Scale probabilities by M and place in two lists, those smaller and those bigger than 1.
n_s = 0 ; n_b = 0
do i=1,M
  A(i) = i          ! Not an arbitrary initialization (*)
  Q(i) = M*P(i)
  if (Q(i)<1) then
    n_s = n_s + 1
    smaller(n_s) = i
  else
    n_b = n_b + 1
    bigger(n_b) = i
  endif
enddo

! For each orbital construct probability of staying on the orbital and the alias of the orbital.
do while (n_s > 0 .and. n_b > 0)
  s = smaller(n_s)
  b = bigger(n_b)
  A(s) = b
  Q(b) = Q(b) + Q(s) - 1
  if (Q(b) < 1) then
    smaller(n_s) = b
    n_b = n_b - 1
  else
    n_s = n_s - 1
  endif
enddo

! (*) Initialize A(i) = i, so that if the random number exceeds a floating point approximation
!    to Q(i) = 1, i is returned (as it should be) rather than an arbitrary initialized state.

```

is a normalization factor. Note that a state which is its own time-reversed partner ($|i\rangle = |i'\rangle$) can only have non-zero coefficients in a wavefunction that has $z = 1$.

In each symmetrized linear combination, $|\tilde{i}\rangle$, one of the states is chosen to be the “representative”, $|i\rangle_{\text{rep}}$. The representative has a positive coefficient in the linear combination, and non-representative state has the same coefficient multiplied by z . In Eq. (E1) $|i\rangle_{\text{rep}} = |i\rangle$. The representative is chosen by converting the computer representation of states (a binary string) into a number and then defining,

$$|i\rangle_{\text{rep}} \equiv \min(|i\rangle, |i'\rangle) \quad (\text{E3})$$

Thus the representative is the state that comes first according to an arbitrary (but consistent) convention for ordering.

Recall that when time-reversal symmetry is not used, a walker that makes an off-diagonal move from state $|i\rangle$ to state $|j\rangle$ is assigned weight, $w_j = \frac{-\tau H_{ji}}{P_{ji}} \left(\frac{w_i}{n_i} \right)$, where w_i and n_i are the weight and number of walkers on $|i\rangle$, respectively. This viewpoint is adopted even with the inclusion of time-reversal symmetry, albeit with modifications

to the Hamiltonian matrix element and the proposal probability, to give,

$$w_{\tilde{j}} = -\frac{\tau \tilde{H}_{\tilde{j}\tilde{i}}}{P_{\tilde{j}\tilde{i}}} \left(\frac{w_{\tilde{i}}}{n_{\tilde{i}}} \right) \quad (\text{E4})$$

where $\tilde{H}_{\tilde{j}\tilde{i}}$ is the Hamiltonian matrix element between the two symmetrized pairs of states, \tilde{i} and \tilde{j} , and $P_{\tilde{j}\tilde{i}}$ is the total probability of making a transition between them.

Since the time-reversal operator and the Hamiltonian commute ($[\hat{T}, \hat{H}] = 0$), it follows that $H_{ji'} = H_{j'i}$, and since $\hat{T}^2 = 1$, $H_{j'i'} = H_{ji}$. Then, using expressions for $|\tilde{i}\rangle$ and $|\tilde{j}\rangle$ from Eq. (E1) we get,

$$\tilde{H}_{\tilde{j}\tilde{i}} = \frac{H_{ji} + zH_{j'i}}{N_i N_j} \quad (\text{E5})$$

To evaluate $P_{\tilde{j}\tilde{i}}$, treat $|i\rangle_{\text{rep}}$ just as the usual (unsymmetrized) state (only consider the usual Hamiltonian connections from $|i\rangle_{\text{rep}}$, not its symmetry related pair state). With probability $P_{j,i_{\text{rep}}}$, state $|i\rangle_{\text{rep}}$ spawns to state $|j\rangle$, which may or may not be its own representative. Since non-representative states are not included in the list of occupied states, if $|j'\rangle \neq |j\rangle$, we must sum over both possibilities to get

$$\begin{aligned} P_{\tilde{j}\tilde{i}} &= P_{j_{\text{rep}}, i_{\text{rep}}} \\ &= P_{j, i_{\text{rep}}} + P_{j', i_{\text{rep}}}. \end{aligned} \quad (\text{E6})$$

Appendix F: Choice of weighting when multiple events lead to a single state

Let P be the matrix element of the projector for a transition between two particular states. Suppose there are N events with probabilities p_i, \dots, p_N that result in this transition. (In general, $\sum_i^N p_i < 1$, since there are other states that can be accessed also.) The probability of getting that state is $\sum_i^N p_i$, so the weight multiplier for this move is $\frac{P}{\sum_i^N p_i}$ regardless of which event led to this state. This prescription is correct since

$$\sum_i^N p_i \frac{P}{\sum_i^N p_i} = P. \quad (\text{F1})$$

(P is independent of i because all the possibilities, i , correspond to the same state.)

There is an alternative approach which avoids the expense of computing the probabilities for the $N - 1$ other events that result in the same state. In this approach, when we pick a particular event, i , the weight multiplier is $\frac{P}{Np_i}$ rather than $\frac{P}{\sum_i^N p_i}$, so it depends on which of the N events was selected. This prescription is also correct since

$$\sum_i^N p_i \frac{P}{Np_i} = P \quad (\text{F2})$$

There is a loss of efficiency, that can be large if the p_i differ greatly from each other. So, there is a trade-off between avoiding the expense of computing the $N - 1$ additional probabilities and the increase in fluctuations of the weights.

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